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Electrocyclic Aromatic Substitution by Nitrile Ylides to give 3*H*-2-Benzazepines: Substituent Effects and Mechanism

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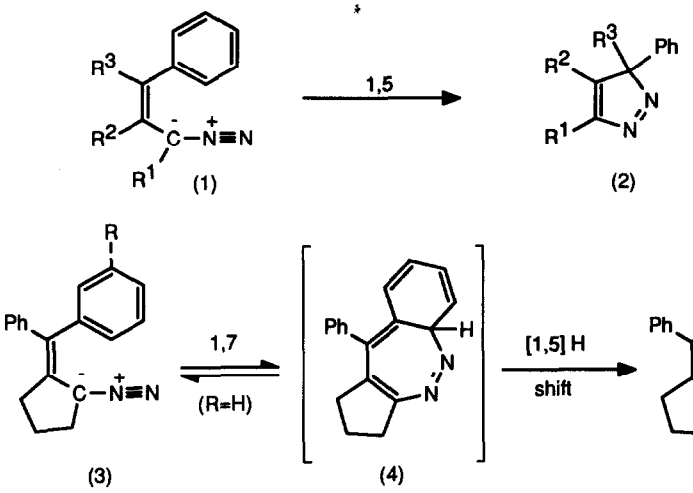
Abstract - Benzonitrile 3,3-diarylallyl nitrile ylides (16), generated by the base-induced dehydrochlorination of imidoyl chlorides, cyclised by 1,7-ring closure to give 3H-2-benzazepines e.g. (19), in contrast to analogous diazo-compounds (1) which prefer 1,5-electrocyclisation. Asymmetrically placed substituents [R in (16b-e)] favour substitution at the ortho (2') position irrespective of their polar electronic effects. Deuterium labelling studies have shown that the cyclisation step is irreversible for these nitrile ylides in contrast to the analogous diazo-compounds (3) for which it is reversible.

INTRODUCTION

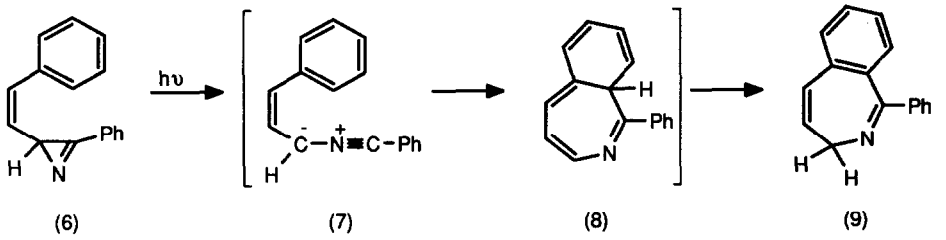
This paper is concerned with the cyclisation reactions of diene-conjugated nitrile ylides of the type (**7**) in which the γ,δ double bond is part of an aryl ring[1]. It follows our earlier work on diazo compounds (**1**) of the same type, Scheme 1, in which it was found that compounds of the type (**1**), containing an unconstrained acyclic olefinic double bond in the α,β position, cyclise exclusively *via* 1,5-electrocyclisation to give as primary products the pyrazoles (**2**)[2]. However, it was also found that the electrocyclisation periselectivity in this system could be readily altered by structural changes, for example the fusion of a cyclopentyl ring at C3/C4 as in (**3**) inhibited the 1,5 cyclisation and completely diverted the course of the reaction into the alternative 1,7 cyclisation path to give the 3*H*-1,2-benzodiazepine system (**5**). Work on the mechanism of this aromatic substitution reaction showed that, under the normal cyclisation conditions at 80°C, the cyclisation step is reversible, followed by a relatively slow, irreversible sigmatropic hydrogen shift.[3] The directive effects of asymmetrically placed substituents [R in (**3**)] were also determined and are noted in Table 1.

In contrast to the 1,5 cyclisation path followed by (**1**), it was shown in later work by Padwa that the analogous nitrile ylide (**7**), generated by the photolysis of the azirine (**6**), cyclised predominantly (>97:3) by 1,7 ring closure to give the 3*H*-2-benzazepine (**9**)[4]. This striking difference in periselectivity between two formally similar reactants which differ only in the nature of the terminal atom of the 1,3-dipole led to the work described here. In view of the fact that the nitrile ylide (**7**) had been generated by a photochemical route and knowing that other work had revealed differences between such reactions and those of analogues generated by 'thermal' methods, the first objective was to determine the periselectivity of systems of this type, (**16a**) in Scheme 3, when generated by a non-photochemical route. This led to work on mechanism and substituent

effects which involved the cyclisation of substituted nitrile ylides, **(16b-e)** in Scheme 4, and their deuteriated analogues, Scheme 5, as described below.



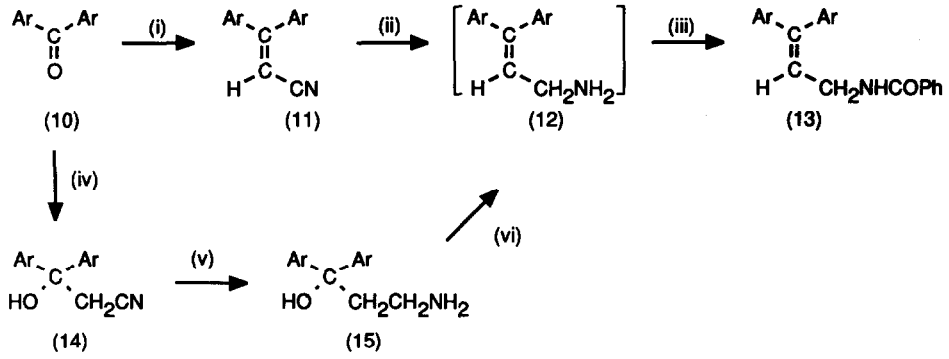
Scheme 1



RESULTS AND DISCUSSION

(i) Synthesis of Reactants.

The nitrile ylides (16) were generated by the well-established general route involving the base induced 1,3-dehydrochlorination of imidoyl chlorides, Scheme 3. The imidoyl chlorides were prepared by reaction of the amides **(13)** with either thionyl chloride or phosphorus pentachloride. The ^{1}H n.m.r. spectra of the crude imidoyl chlorides confirmed that cyclisation had not taken place at this stage. The amides themselves were synthesised *via* the two paths shown in Scheme 2. In Method A, carrying out the reduction of the nitrile [step (ii)] at low temperature (-45^{o}C) effectively prevented concomitant reduction of the double bond when the aromatic substituent was H, Me, and MeO. However it was not possible, even at lower temperatures, to prevent the full reduction when the substituent was CF_3 or Cl, and the alternative route, Method B, was used instead. It seems likely that the reactivity of the double bond in **(11)** to reduction is enhanced by these electron withdrawing substituents in the aromatic ring. The amines **(12)** and **(15)** were used without purification but the nitriles **(11)** and **(14)**, and the amides **(13)** were characterised by elemental analysis or accurate mass measurement, Table 3, and by their ^{1}H n.m.r. spectra, Table 4.



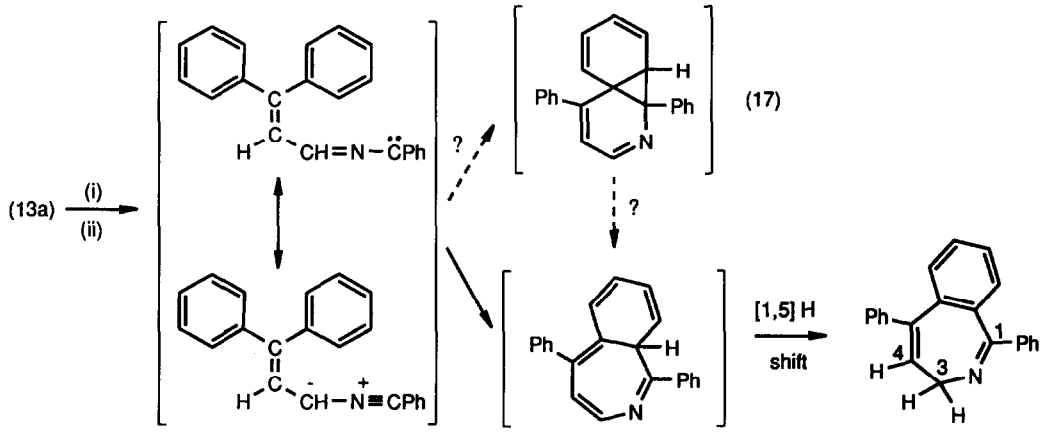
Method A (i) $(EtO)_2POCH_2CN$ / NaH / DME, (ii) $LiAlH_4$ / -45°C / ether, (iii) PhCOCl

Method B (iv) CH_3CN / BuLi, (v) $LiAlH_4$ / 0°C, (vi) H^+

Scheme 2

(ii) Nitrile Ylide Cyclisations.

These reactions, Scheme 3-5 were carried out in THF at either room temperature or 0°C using potassium *tert*-butoxide as the base[5]. The addition of the base produced a deep purple coloration which faded over *ca* 15 minutes after which the reaction mixture was kept at room temperature for several hours before work up.



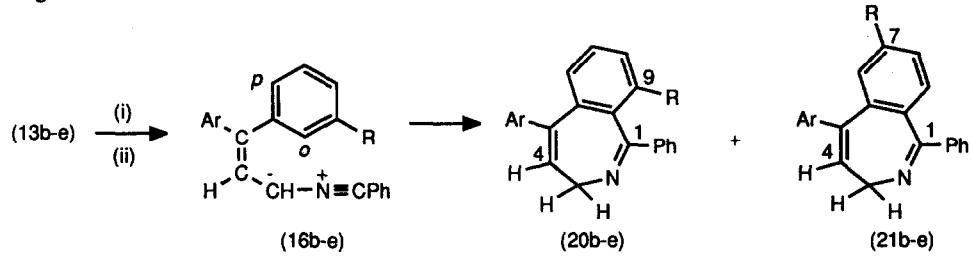
(i) PCl_5 or $SOCl_2$
(ii) $KOBu^t$ / THF

Scheme 3

a) The unsubstituted case (16a). Cyclisation of the unsubstituted nitrile ylide **(16a)**, Scheme 3, gave 1,5-diphenyl-3*H*-2-benzazepine **(19)** in 73% yield after purification. Its ^1H n.m.r. spectrum was typical of the series and at 0°C characteristically showed the C-3/C-4 protons as an ABX system with the C-3 methylene protons as doublets of doublets at δ 3.10 and 4.48 (J_{AB} 10.3Hz) and H-4 as a triplet at δ 6.50. Seven-membered ring systems of this type generally undergo ring inversion at a rate which can be studied by variable temperature n.m.r.[6] and, on heating, the methylene absorptions of **(19)** broadened and coalesced (T_c 77°C) as expected. This corresponds to an activation energy for ring inversion of 67.4±0.4 kJ $mole^{-1}$ which is *ca* 25

kJmol^{-1} higher than for a monocyclic analogue[7]. This difference almost certainly results from steric interactions in (**19**) between the 1- and 5-phenyl groups and the adjacent hydrogens of the fused benzene ring.

(b) The substituted nitrile ylides (16b-e). Having thus confirmed that the cyclisation periselectivity in these conjugated nitrile ylides is indeed different to that in the analogous diazo-compounds (**1**), it was decided to investigate the reactions of the nitrile ylides further in the hope of discovering an explanation. *A priori* it seemed possible that the difference was due to the operation of a different reaction mechanism. For example, given the known propensity of nitrile ylides to undergo carbene-type 1,1-cycloaddition reactions[4,8], it is possible that the first step is a cycloaddition reaction of this type to give (**17**), Scheme 3, rather than an electrocyclisation to give (**18**). It was therefore decided to attempt to detect such a difference in mechanism by carrying out a study of the directing effect of asymmetrically placed substituents, Scheme 4. In these reactions the two isomeric products (**20**) and (**21**) are formed by cyclisation *ortho* or *para* to the substituent R (these are referred to subsequently as the *ortho* and *para* products). The transition states for the electrocyclisation and the carbene-type mechanisms have been discussed in detail elsewhere[8]. Since they require different orbital interactions and are quite different in nature and it was thought likely that substituents in the aromatic ring would affect their reaction rates, and hence the *ortho*/*para* ratio, in different ways. Major differences from the results of the earlier parallel work on diazo cyclisations[3], given for comparison in Table 1, would be taken as indicating a difference in mechanism.



Scheme 4

The n.m.r. spectra of the crude products from these reactions showed that the yields were very high but purification proved to be difficult as chromatography on silica gel resulted in much decomposition. Attempts to measure the isomer ratios by h.p.l.c. on silica, alumina and reverse-phase silica (ODS) were also unsuccessful due to decomposition on the column. However, it was possible in all cases to obtain small samples of the two isomers by preparative t.l.c. on phosphate buffered silica. They were identified *via* accurate mass measurement and by their n.m.r. spectra (Table 5) as discussed in individual cases below. All the proton spectra showed the characteristic ABX pattern for the C-3/C-4 protons. In the cases where R=Me, OMe, and CF_3 the 7- and 9-substituted isomers, (**21**) and (**20**) respectively, were differentiated principally by the chemical shift of the R group attached to the fused benzene ring, based upon the differences expected from the structures and previously observed in the analogous diazepines[3] (for which there was other strong structural evidence). Thus for example in the case where R=Me the isomer which gave Me absorptions at δ 2.34 and 2.35 was formulated as the 7-methyl isomer (**21b**), and the one with Me absorptions at δ 2.00 and 2.34 as the 9-methyl isomer (**20b**). The 9-methyl group in the latter is selectively shielded by its proximity to the face of the phenyl

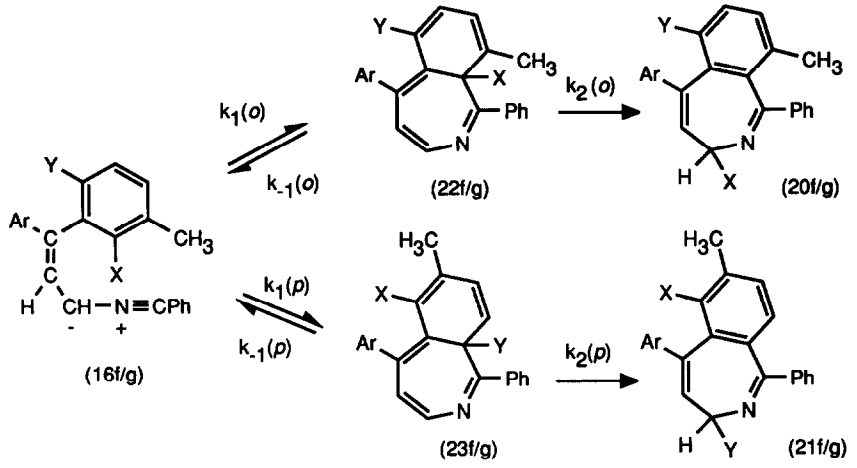
substituent in the 1-position. Steric interaction of the latter with the adjacent methyl group causes it to prefer a conformation in which it is twisted out of the plane of the imine function in the azepine ring and into an orientation in which the 9-methyl group is exposed to the shielding effect of its π-system. The effect of this interaction is also seen in the chemical shift of the *ortho* protons of the phenyl group; in **(21b)** they are deshielded by the imine group of the azepine ring (see Table 5) while in **(20b)** the phenyl is twisted out of conjugation with the imine group and the deshielding is not seen. The compounds **(20c, R=OMe)** and **(20d, R=CF_3)** similarly showed selective shielding of the 9-R substituent. The differentiation in the case in which R=Cl is based on data obtained for the three cases discussed above on the relative chemical shifts of the 4-H, and on the difference in the ease of ring inversion of the two isomers. The 4-H absorption was found to be more deshielded in the 9-R isomer for all three cases (R=Me, OMe, CF_3), and the activation energy for ring inversion was lower for the 7-R isomers. This latter conclusion is based on the ^{1}H n.m.r. spectra of each pair, run at the same temperature; in these the 7-R isomers showed the C-3 methylene absorptions as broad peaks whereas the 9-R isomers gave sharp multiplets (not enough sample was available for full VT studies). This is consistent with the expectation that the activation energy for ring inversion would be raised by steric interaction between the 9-R group and the adjacent 1-phenyl substituent in **(20)**. For the isomer pair in which R=Cl, the isomer which had the more deshielded 4-H *and* the sharp C-3 methylene multiplets was therefore assigned as the 9-Cl isomer **(20e)** and the other, which had broad C-3 methylene absorptions as the 7-Cl isomer **(21e)**. In all cases the *ortho*/*para* isomer ratio was determined by ^{1}H n.m.r. spectroscopy on the crude product mixture before chromatography using the integrals of the H-4 triplet aborptions in the region δ 6.4 - 6.8. Two or three reactions were carried out for each substituent and the results are given in Table 1. They will be discussed below in the context of the mechanism of the cyclisation.

Table 1 Substituent Directive Effects in the Cyclisation of (16b-e)

Directive Effect -	*o* / *p* ratio			
R	Me	MeO	Cl	CF_3
Nitrile Ylide (16)	2.5	1.5	2.1	1.5
Diazo-compound (3)[3]	3.6	1.8	2.7	0.64
Radical phenylation[9]	2.6	2.8	2.1	0.73
Electrophilic chlorination[10]	1.6	0.27	0.29	1.9

(c) Deuterium labelled nitrile ylides (16f) and (16g). The mechanism of the cyclisation of diazo-compound (3), Scheme 1, was investigated earlier *via* the use of substrates selectively deuteriated at the cyclisation site and it was concluded that the cyclisation step was reversible under the normal cyclisation conditions at 80°C[3]. This section is concerned with the application of similar techniques to the analogous nitrile ylide reaction *via* the cyclisation of the species **(16f)** and **(16g)**, Scheme 5, which are selectively deuteriated in the positions *ortho* and *para* respectively to the methyl substituent. In these systems the presence of the deuterium will have a significant effect only when it is the migrating species in the second step, the rate of which will be diminished by the k_H/k_D primary isotope effect. In the cyclisation of **(16f)** this would therefore affect the rate of formation of only the *ortho* product **(20f)**, and in the case of **(16g)** only the *para* product **(21g)**. If the first

step is reversible ($k_{-1}>0$) this would result in the diversion of the reaction to favour cyclisation at the non-deuteriated site. Such diversions were observed for the analogous diazo cyclisation (Table 2). However, if the cyclisation step is not reversible ($k_{-1}<<k_2$) then the product ratio should be unaffected by the presence of the deuterium, except for a relatively small secondary isotope effect in the cyclisation step.



for all compounds (f), X=D, Y=H, Ar=2'-D-3'-Me-C_6H_3-
for all compounds (g), X=H, Y=D, Ar=6'-D-3'-Me-C_6H_3-
D=^{2}H

Scheme 5

The objective here was therefore to generate the nitrile ylides **(16f)** and **(16g)** and measure the product ratio in each case. The precursor deuteriated amides **(13f)** and **(13g)** were prepared by the usual route and found by low eV mass spectrometry, Table 4 , to contain respectively 92% and 94% of the required dideuteriated species. The cyclisations were carried out in the usual way and the mixture of *ortho* and *para* products was separated from unreacted starting material and from by-products by chromatography on deactivated alumina. These mixtures were used in the determination of the product ratios by ^{1}H and ^{2}H n.m.r. spectroscopy as discussed below. The *ortho* and *para* isomers **(20f and g)**, **(21f and g)** were then separated by preparative t.l.c. and identified by their ^{1}H n.m.r. spectra (Table 5) and by exact mass measurement. The ^{1}H n.m.r. spectra of compounds **(20f)** and **(21g)** confirmed the presence and location of the deuterium atoms, both gave integrals for the C-3 methylene group of *ca* one proton only (equally distributed between the 'axial' and 'equatorial' locations), and in both compounds the 4-H absorption was a doublet instead of the triplet of the non-deuteriated analogue.

The *ortho*/*para* ratios were determined as usual from the ^{1}H n.m.r. spectra of the mixtures using the integral ratio of the 4-H absorptions - triplets for **(20g)** and **(21f)** and doublets for **(20f)** and **(21g)** as noted above. Duplicate experiments were carried out for the cyclisation of both **(16f)** and **(16g)** and the results are given in Table 2. In addition the isomer ratios were also determined from the ^{2}H n.m.r. spectra of the product mixtures using the ratio of the integrals due to the aliphatic and aromatic deuterons[3]. The concordance between the duplicate experiments in the latter determinations was not very high due to the width of the deuterium signals and the consequent difficulty in measurement of the integrals, but the average results as shown in Table 2 are close to those from the ^{1}H spectra. The *ortho*/*para* ratios measured in these experiments differ little from the ratio for the undeuteriated analogue **(16b)** and certainly do not show the considerable diversions in the

course of the reaction which were observed for the analogous diazo cyclisations. It is therefore concluded that the cyclisation step is irreversible in the nitrile ylide reaction. However it must be noted that, while this is true for the methyl substituted nitrile ylide **(16b)**, it is not necessarily so in the case of other substituents.

Table 2 The Effect of Deuterium Substitution on the Cyclisation of (16f) and (16g)

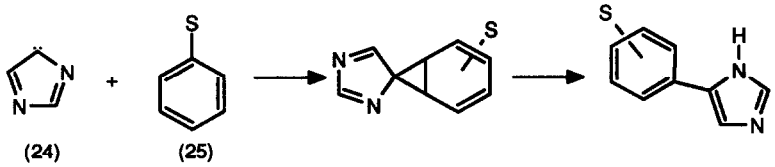
	o /*p* ratio		
Nitrile Ylide	no ^2H	*o*-^2H	*p*-^2H
(16b)	2.5		
(16f)		2.4[a]	
(16g)			2.1[b]
Diazo-compound (3)	3.6	0.99	13.4

a. 2.37±0.15 from ^1H spectra and 2.36±0.31 from ^2H spectra.
b. 2.09±0.03 from ^1H spectra and 2.05±0.25 from ^2H spectra.

(iii) The Mechanism of the Cyclisation.

The results above show that the cyclisation step is irreversible for the nitrile ylides **(16)** whereas it is reversible for the diazo-compounds **(3)**. The explanation for this probably lies in the formation of a stronger C-C bond in the nitrile ylide cyclisation rather than the weaker C-N bond in the case of the diazo-compound (bond energies *ca* 80 and 62 kcal mol^{-1} respectively). This result makes the interpretation of the *ortho* / *para* selectivity data shown in Table 1, easier in this case than it was for the diazo analalogues, since it is clear that the selectivity must arise from the effect of the substituent (R) in the cyclisation step only. In the diazo cyclisations it could have been due in part to an effect on the rate of the second step, the sigmatropic hydrogen migration. The information to be gained by comparing the data from the two dipoles is therefore rather limited, but it is interesting that the results are similar in the cases where R=Me, MeO, and Cl which all show a preference for attack at the more hindered *ortho* position. Presumably in these cases the effect of the substituent on the rate of the sigmatropic shift in the diazo cyclisation is small and the product ratio is controlled largely in the cyclisation step. In the case of the substituent CF_3 the diazo group showed a modest preference for *para* attack while the nitrile ylide again preferred the *ortho* position. As yet we have no explanation for this 'ortho directing' effect seen in both the diazo and nitrile ylide cyclisations. However in the context of this paper the key point is whether these data can be used to differentiate between the two cyclisation mechanisms set out in Scheme 3. Part of the difficulty in this lies in estimating the polar character of the terminal carbon of the nitrile ylide when it is reacting in carbene-type 1,1-cycloadditions. If it is truly carbene-like i.e. electrophilic in nature, then the selectivity predicted should resemble that seen in other electrophilic aromatic substitution reactions. Data are given in Table 1 on the *ortho* / *para* ratios obtained in two other types of aromatic substitution, radical phenylation[9] and electrophilic chlorination[10]. The results for the nitrile ylide for R=Cl and MeO are clearly different to those for electrophilic substitution. The work by Shechter[11] on directive effects in aromatic substitution by the carbene **(24)** is also relevant. This carbene showed the expected electrophilic properties and the result for S=Cl in the substrate **(25)**, which strongly promoted *para* substitution *(via* addition

to the 3,4 position of the aromatic ring) is quite different to that for the cyclisation of the analogous nitrile ylide (**16e**).



(24) (25)

From these comparisons it is thought unlikely that the nitrile ylide cyclisation proceeds *via* a carbene-type 1,1-cycloaddition to give (**17**). The similarity between the data for 1,3-dipolar aromatic substitution and that for radical phenylation is interesting and in general way supports the conclusion that the attacking entity is not strongly polarised in the 1,3-dipole reactions.

The original point at issue, the difference in the electrocyclisation periselectivity between the unconstrained diazo-compounds of type (**1**) and the nitrile ylide analogues (**7**)/(**16**) does not therefore seem to be due to the operation of a different reaction mechanism in the 1,7 ring closure. It is more likely that it is due to differences in the structure and properties of the two 1,3-dipoles which affect the relative activation energies for the 1,5- and the 1,7-modes of ring closure. The mechanisms and transition states for these two modes of cyclisation have been discussed elsewhere[12, 8], and from these it seems likely that the difference in periselectivity between the two 1,3-dipoles is largely due to the steric effect of the phenyl substituent on the 'attacking' carbon atom of the nitrile ylide. This bulky group would make the transition states for both modes of cyclisation more crowded than those for the analogous diazo-compound but the effect would be greater for the 1,5 cyclisation thus selectively disfavouring this reaction path. The difference in the ease of in-plane bending of the two 1,3 dipoles is probably also important since the transition state for 1,5-electrocyclisation must require more bending of the dipole than that for 1,7-electrocyclisation. In-plane bending disrupts and weakens the orthogonal π-bond between the N and the terminal atom of the dipole (N in the diazo-group and C in the nitrile ylide) and it might be expected that bending of the former, involving disruption of a relatively weak N=N, would be easier than bending the nitrile ylide with the disruption of the stronger N=C. This is in accord with the observed preference for 1,5 ring closure by the diazo-compounds in these systems.

EXPERIMENTAL SECTION

Solvents, Reagents and Starting Materials.

1,2-Dimethoxyethane was dried over potassium hydroxide, distilled from calcium hydride and stored over molecular sieve 4A. Tetrahydrofuran (THF) was freshly distilled from calcium hydride and then lithium aluminium hydride as required. Unless otherwise stated 'petroleum ether' refers to the fraction b.p. 40-60 °C. The following were prepared by literature routes and had the reported physical and spectroscopic properties: 3,3-diphenylpropenenitrile (**11a**)[13], 3-methylbenzoyl chloride[14], 3-methoxybenzoyl chloride[15], 3,3'-dichlorbenzophenone (**10e**)[16]. 3,3'-Bis(trifluoromethyl)benzophenone (**10d**) was obtained from Aldrich Chemical Company. 2-Deuterio-3-bromotoluene and 4-deuterio-3-bromotoluene[3] were respectively 92% and 93% monodeuteriated.

Preparation of *N*-Benzoyl-3,3-diarylprop-2-en-1-ylamines (13a-g)

(i) ***Substituted Benzophenones (10). 3,3'-Dimethylbenzophenone (10b).*** The Grignard reagent from 3-bromotoluene (10.3 g, 60 mmole) in THF (50 ml) was added over *ca* 1h by transfer with a double tipped needle to a solution of 3-methylbenzoyl chloride (18.6 g, 0.12 mol) in THF (30 ml) kept at -78°C. The

mixture was kept at room temperature overnight and quenched by the addition of water (150 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 x 30 ml). The combined organic layers were washed with 5M aqueous sodium hydroxide (2 x 50 ml) and brine (2 x 50 ml). Drying, evaporation, and chromatography on alumina (petroleum ether:ethyl acetate 1: 0 -> 1: 1) gave a colourless oil which was distilled to give 3,3'-dimethylbenzophenone **(10b)** (8.7 g, 68%) b.p. 130-132°C at 0.5mmHg, m.p. 39-42°C (lit.[17], b.p. 230-235°C at 20mmHg, m.p. 45°C.

*3,3'-Dimethoxybenzophenone **(10c)*** (70%) b.p. 140-145°C at 0.3mmHg (lit.[17], 144-145°C at 0.3mmHg) was prepared by a similar route.

*2,2'-Dideuterio-3,3'-methylbenzophenone **(10f)*** (49%), prepared by the method of Michael and Hornfeld[18], had b.p. 132-136°C at 0.1mmHg (Found m/z 212.1170. $C_{15}H_{12}{}^{2}HO$ requires m/z 212.1170).

*6,6'-Dideuterio-3,3'-methylbenzophenone **(10g)*** (38%), prepared by the same route, had b.p. 180-185°C at 13mmHg (Found m/z 212.1170. $C_{15}H_{12}{}^{2}HO$ requires 212.1170).

(ii) ***Substituted 3,3-Diarylpropenenitriles (11a-d, f,g).*** These were prepared from the appropriate substituted benzophenone by the method of Maisey[13]. Their yields and physical and spectroscopic characteristics are given in Tables 3 and 4.

(iii) ***Substituted 3-Hydroxy-3,3-diarylphenylpropanenitriles (14d and e).*** These were prepared by the method of Kaiser and Hauser[19] and purified by dry column flash chromatography. Their yields and physical and spectroscopic properties are given in Tables 3 and 4.

(iv) ***N-Benzoyl-3,3-diarylprop-2-en-1-ylamines (13a-g). Method A.*** Compounds **(12a, b, c, f, g)** were prepared by reduction of the corresponding nitrile to the amine with lithium aluminium hydride at -45°C in ether using an adaptation of the method of Maisey[13]. The amines were unstable and decomposed on attempted purification and were therefore converted directly into the required amides. The yields and the physical and spectroscopic properties of the products are given in Tables 3 and 4. The method is given in detail for the first example.

*N-Benzoyl-3,3-diphenylprop-2-en-1-ylamine **(13a).*** 3,3-Diphenylpropenenitrile (11a) (5.0 g, 24.4 mmol) in ether (30 ml) was added dropwise to a suspension of lithium aluminium hydride (3.5 g, 92 mmol) in ether at -45°C under an atmosphere of nitrogen. The mixture was stirred at -45° for 10 h before quenching at -45° with saturated aqueous sodium sulphate. After allowing the mixture to warm up to room temperature overnight the organic phase was separated and the aqueous phase extracted with ether (3 x 50 ml). The combined organic layers were dried and evaporated to give the crude amine **(12a)** (4.75 g). A mixture of this product, benzene (70 ml), pyridine (10 ml), and benzoyl chloride (5.3 ml, 6.4 g, 45.7 mmol) was heated under reflux for 45 min, cooled and poured into water (250 ml). Work-up followed by dry column flash chromatography (petroleum ether : ethyl acetate 100 : 0 -> 30 : 70) and crystallisation from ethanol gave *N*-benzoyl-3,3-diphenylprop-2-en-1-ylamine **(13a)** (3.62 g, 47%).

Method B. Compounds **(13d)** and **(13e)** were prepared by successive reduction, dehydration and benzoylation of the 3-hydroxy-3,3-diarylpropanenitriles **(14d)** and **(14e)** repectively. The method is given in detail for the first example.

*N-Benzoyl-3,3-bis(3'-trifluoromethylphenyl)prop-2-en-1-ylamine **(13d).*** 3-Hydroxy-3,3-bis(3'-trifluoromethylphenyl)propanenitrile **(14d)** (1.79 g, 4.98 mmol) in ether (10 ml) was added with stirring to a suspension of lithium aluminium hydride (0.57 g, 15 mmol) in ether (25 ml) under nitrogen at 0°C. The mixture was stirred for 30 min at 0°C and 90 min at room temperature, quenched at 0°C by the slow addition of water, and then poured into aqueous sodium hydroxide (10% w/v) (25 ml). Separation, extraction of the aqueous phase with ether (3 x 10 ml), drying, and evaporation gave the crude hydroxy-amine **(15d)** (1.68 g, 93%) as a pale yellow oil. This oil in trifluoroacetic acid (35 ml) was boiled under reflux under nitrogen for 48 h. After evaporation of the solvent the residue was treated with aqueous sodium hydroxide (20% w/v) (20 ml) and extracted into ether (3 x 20 ml). Drying and evaporation gave the crude unsaturated amine **(12d)** as a

brown oil (1.36 g). A mixture of the whole product in dichloromethane (7 ml) with aqueous sodium bicarbonate (sat.) (7 ml) and benzoyl chloride (0.5 ml, 0.61 g, 4.33 mmol) was stirred at room temperature for 22 h. Work-up, dry flash chromatography (petroleum ether : ether 100 : 0 -> 30 : 70), and crystallisation from petroleum ether / toluene gave *N*-benzoyl-3,3-bis(3'-trifluoromethylphenyl)prop-2-en-1-ylamine **(14d)** (1.14 g, 62%).

The properties of the compounds prepared by these routes are given in Tables 3 and 4.

Table 3 Yields and Physical Data on the Diarylpropenenitriles (11) and (14) and the Amides (13)

Comp.	Yield (%)	M.p. (°C)(solv.[1]) or b.p. (°C/mmHg)	Molecular formula	C(%) Found Calc.	H(%) Found Calc.	N(%) Found Calc.	m/z (M^+) Found Calc.
(11b)	77	m.p. 58-60 (PE)	$C_{17}H_{15}N$	87.6	6.5	6.0	
				87.5	6.5	6.0	
(11c)	87	b.p. 202-204/0.1	$C_{17}H_{15}NO_2$				265.1100
							265.1103
(11d)	86	b.p. 194-196/0.2	$C_{17}H_9F_6N$	60.1	2.6	4.2	341.0639
				59.8	2.7	4.1	341.0639
(11f)	60	b.p. 175-179/0.6	$C_{17}H_{13}{}^2H_2N$				235.1327
							235.1330
(11g)	99	b.p. 160-164/0.1	$C_{17}H_{13}{}^2H_2N$				235.1331
							235.1330
(14d)	91	oil, not distilled	$C_{17}H_{11}NOF_6$				359.0733
							359.0745
(14e)	39	100-101 (PE)	$C_{15}H_{11}Cl_2NO$	61.4	3.7	4.8	293.0181
				61.85	3.8	4.8	293.0188
(13a)	47	m.p. 145-146.5 (E)	$C_{22}H_{19}NO$	84.2	6.2	4.3	313.1458
				84.3	6.1	4.5	313.1467
(13b)	55	oil, not distilled	$C_{24}H_{23}NO$				341.1784
							341.1780
(13c)	64	oil, not distilled	$C_{24}H_{23}NO_3$				373.1681
							373.1678
(13d)	62	114.5-115.5 (PE/T)	$C_{24}H_{17}NOF_6$	64.4	3.8	3.2	
				64.1	3.8	3.1	
(13e)	73	121-122.5 (PE/T)	$C_{22}H_{17}NOCl_2$	69.3	4.5	3.6	
				69.3	4.5	3.7	
(13f)	58	oil, not distilled	$C_{24}H_{21}{}^2H_2NO$				343.1911
							343.1905
(13g)	52	oil, not distilled	$C_{24}H_{21}{}^2H_2NO$				343.1900
							343.1905

1. E=ethanol, M=methanol, PE=petroleum ether b.p. 60-80°C, T=toluene

Generation and Reactions of Benzonitrile 3,3-Diarylallyl Ylides (16a-g).

In the following reactions the imidoyl chlorides **(16a-g)** were prepared by reaction of the amides **(13a-g)** with either phosphorus pentachloride or thionyl chloride and used directly, without purification, after removal of volatile materials on a rotary evaporator. The crude imidoyl chloride was then dissolved in THF and potassium *tert*-butoxide was added at room temperature or 0°C in a single batch. In cases where two isomers were formed their ratio was determined by ^1H n.m.r. spectroscopy on the crude product mixture after initial work-up but before chromatography. The isomers were then separated by flash chromatography on 10% deactivated neutral alumina (petroleum ether : ether, 100 : 0 -> 50 :50) followed by preparative t.l.c. on phosphate buffered (pH 8) silica (petroleum ether : ether, 50 : 50). The first reaction only is described in detail. The spectroscopic

Table 4 Spectroscopic Data for Diarylpropenenitriles (11), and (14) and Amides (13)

		NMR and IR data and Mass spectra
(11b)	δH	2.31(d, J 0.5 Hz, 3H), 2.35 (d, J 0.5 Hz, 3H), 5.66 (s, 1H), 7.05-7.28 (m, 8H)
	υ_{max}	2210 (CN)
(11c)	δH	4.04 (s, 3H), 4.08 (s, 3H), 6.00 (s, 1H), 7.09-7.66 (m, 8H)
	υ_{max}	2210 (CN)
(11d)	δH	5.88 (s, 1H), 7.41-7.80 (m, 8H)
	δF	-62.53, -62.59
	υ_{max}	2220 (CN)
(11f)	δH	2.34 (s, 3H), 2.38 (s, 3H), 5.69 (s, 1H), 7.06-7.38 (m, 6H)
	υ_{max}	2210 (CN)
(11g)	δH	2.34 (s, 3H), 2.38 (s, 3H), 5.69 (s, 1H), 7.10-7.31 (m, 6H)
	υ_{max}	2210 (CN)
(14d)	δH	3.30 (s, 2H), 3.32 (br s, OH), 7.46-7.71 (m, 8H)
	υ_{max}	2260 (CN), 3420 (OH)
(14e)	δH	3.11 (br s, OH), 3.23 (s, 2H), 7.21-7.40 (m, 8H)
	υ_{max}	2259 (CN), 3423 (OH)
(13a)	δH	4.15 (dd, J 6.9 and 5.7 Hz, 2H), 6.18 (t, J 6.9 Hz, 1H), 6.30 (br, NH), 7.18-7.52 (m, 13H), 7.72-7.76 (m, 2H)
	m/z	314 (17%), 313 (68), 208 (19), 193 (18), 192 (100), 146 (16), 122 (19), 105 (91), 103 (19), 77 (53)
	m/z[1]	313 (100), 314 (24.8), 315 (7.6).
	υ_{max}	3300 (NH), 1625 (C=O)
(13b)	δH	2.31 (s, 3H), 2.36 (s, 3H), 4.15 (dd, J 6.8 and 5.7 Hz, 2H), 6.16 (t, J 6.8 Hz, 1H),6.25 (br, NH), 7.00-7.49 (m, 11H), 7.72-7.76 (m, 2H)
	m/z	341 (23%), 236 (21), 221 (12), 220 (52), 210 (39), 202 (30), 121 (22), 119 (91), 105 (100), 91 (34), 77 (58)
	m/z[1]	341 (100), 342 (30.4), 343 (23.9), 344 (6.6).
	υ_{max}	3310 (NH), 1635 (C=O)
(13c)	δH	3.71 (s, 3H), 3.73 (s, 3H), 4.14 (t, J 6.2 Hz), 6.18 (br, 2H), 6.73-6.89 (m, 6H), 7.12-7.44 (m, 5H), 7.73-7.78 (m, 2H)
	m/z	374 (40%), 269 (40), 253 (100), 148 (51), 147 (45), 136 (87)
	υ_{max}	3320 (NH), 1640 (C=O)
(13d)	δH	4.13 (dd, J 6.8 and 5.8 Hz, 2H), 6.27 (t, J 6.8 Hz, 1H), 6.53 (br, NH), 7.25-7.62 (m, 11H), 7.73-7.78 (m, 2H)
	δF	-62.30
	m/z	449 (36%), 328 (18), 146 (10), 122 (18), 105 (100)
	υ_{max}	3320 (NH), 1630 (C=O)
(13e)	δH	4.11 (br t, J ca 6.6 Hz, 2H), 6.18 (br t, J ca 6.7 Hz, 1H), 6.46 (br, NH), 7.02-7.49 (m,11H), 7.73-7.77 (m,2H)
	m/z	383 (16%), 381 (22), 245 (21), 151 (25), 149 (29), 146 (67), 123 (24), 122 (100), 105 (99), 102 (26), 91 (31), 77 (61), 51 (45), 43 (58)
	υ_{max}	3260 (NH), 1625 (C=O)
(13f)	δH	2.30 (s, 3H), 2.35 (s, 3H), 4.15 (dd, J 6.9 and 5.6 Hz, 2H), 6.15 (t , J6.9 Hz, and br, NH, 2H), 7.00-7.53 (m, 9H), 7.71-7.76 (m, 2H)
	δ^2H	7.05, 7.13
	m/z[1]	341 (8.95), 342 (13.7), 343 (100), 344 (31.1), 345 (18.9). % Dideuteriation = 91.7.
	υ_{max}	3310 (NH), 1640 (C=O)
(13g)	δH	2.30 (s, 3H), 2.35 (s, 3H), 4.14 (dd, J 6.9 and 5.7 Hz, 2H), 6.15 (t, J6.9 Hz, and br, NH, 2H), 7.00-7.49 (m, 9H), 7.70-7.75 (m, 2H)
	δ^2H	7.05
	m/z[1]	341 (6.7), 342 (12.2), 343 (100), 344 (32.5), 345 (18.8). % Dideuteriation = 93.8.

1. Average of six runs at low eV.

Table 5 Spectroscopic Data for the 3*H*-2-Benzazepines (19), (20), (21)

	R		NMR data and Mass spectra
(19)	-	δH (0°C)	3.10 (dd, J 10.3 and 6.7 Hz, 1H), 4.48 (dd, J 10.3 and 7.3 Hz, 1H), 6.50 (br t, J ca 6.8 Hz, 1H), 7.07-7.70 (m,14H).
		T_c	350 K (hexachlorobutadiene)
		δC	49.1 (CH_2), 125.8 (CH), 127.5 (CH), 127.9 (2 x CH), 128.2 (2 x CH), 128.6 (CH), 128.8 (2 x CH), 129.2 (CH), 129.5 (3 x CH), 130.0 (2 x CH), 137.1, 140.5, 140.9, 141.2, 143.7 (all quat.), 168.8 (quat., C=N)
		m/z	296 (23%), 295 (100), 294 (100), 191 (20), 189 (28), 165 (28), 146 (24), 91 (24), 77 (20)
(21b)	CH_3	δH (-10°C)	2.34 (s, 3H), 2.35 (s, 3H), 3.09 (dd, J 10.2 and 6.8 Hz, 1H), 4.46 (dd, J 10.2 and 7.3 Hz, 1H), 6.44 (br t, J ca 7.0 Hz), 7.05-7.50 (m, 10H), 7.52-7.56(m, 2H)
		δC	49.1 (CH_2), 168.8 (quat., C=N) from spectrum of mixture
		m/z	[mix. with 20b] 323 (39%), 322 (41), 199 (82), 184 (100), 183 (33), 128 (29), 91 (21), 86 (59),84(78)
(20b)	CH_3	δH (-10°C)	2.00 (s, 3H), 2.34 (s, 3H), 3.08 (dd, J 10.0 and 6.5 Hz, 1H), 4.43 (dd, J 10.0 and 7.1 Hz, 1H), 6.56 (br t, J ca 6.8 Hz, 1H), 7.07-7.44 (m, 12H)
		δC	21.3 (CH_3), 22.3 (CH_3), 49.4 (CH_2), 125.9 (CH), 126.4 (CH), 127.8 (2 x CH), 128.0 (2 x CH), 128.1 (CH), 128.3 (2 x CH), 129.0 (CH), 129.1 (CH), 129.4 (CH), 130.5 (CH), 136.5 , 136.8, 137.7, 140.1,141.3, 141.4, 144.2, (all quat.). 167.6 (C=N)
		m/z	see (21b)
(21c)	MeO	δH	3.79 (s, 3H), 3.81 (s, 3H), 3.28 (br, 1H), 4.70 (br, 1H), 6.47 (t, J 7.0 Hz, 1H), 6.81-6.97 (m, 5H), 7.24-7.80 (m, 7H)
		m/z	[mixture with (20c)] 355 (3%), 354 (3), 242 (21), 135 (45), 121 (32), 105 (84), 88 (43), 86 (87), 84 (73), 77 (75), 57 (30), 51 (33), 49 (70), 47 (100)
(20c)	MeO	δH	3.51 (s, 3H), 3.79 (s, 3H), 3.15 (dd, J 10.2 and 6.6 Hz, 1H), 4.48 (dd, J 10.2 and 7.2 Hz, 1H), 6.55 (br t, J 6.8 Hz, 1H), 6.82-7.03 (m, 5H), 7.20-7.51 (m, 7H)
		m/z	see (21c)
(21d)	CF_3	δH	3.13 (br, 1H), 4.59 (br, 1H), 6.63 (t, J 6.8 Hz, 1H), 7.38-7.65 (m, 12H)
		δF	-62.41 (s, 3F), -62.66 (s, 3F)
		m/z	[mixture with (20d)] 431 (51%), 430 (100), 105 (43), 85 (42), 83 (62)
(20d)	CF_3	δH	3.13 (dd, J 10.2 and 6.4 Hz, 1H), 4.59 (dd, J 10.2 and 7.1 Hz, 1H), 6.75 (br t, J 6.5 Hz, 1H), 7.25-7.63 (m, 12H)
		δF	-56.69 (s, 3F), -62.39 (s, 3F)
		m/z	see (21d)
(21e)	Cl	δH	3.09 (br, 1H), 4.53 (br, 1H), 6.51 (t, J 6.9 Hz, 1H), 7.11-7.63 (m, 12H)
		m/z	[mixture with (20e)] 366 (15%), 365 (29), 364 (72), 363 (48), 362 (100), 189 (10), 146 (21)
(20e)	Cl	δH	3.13 (dd, J 10.2 and 6.7 Hz, 1H), 4.52 (dd, J 10.2 and 7.3 Hz, 1H), 6.64 (br t, J 6.9 Hz, 1H), 7.14-7.45 (m, 12H)
		m/z	see (21e)
(20f)	-	δH	2.01 (s, 3H), 2.34 (s, 3H), [3.08 (d, J 6.4 Hz) and 4.42 (d, J 7.1 Hz), 1H], 6.56 (d, J 6.7 Hz, 1H), 7.06-7.47 (m, 10H)
		m/z	325 (48%), 324 (100), 149 (26), 142 (14), 111 (10), 105 (10)
(21f)	-	δH	2.34 (s, 3H), 2.35 (s, 3H), 3.10 (br, 1H), 4.45 (br, 1H), 6.43 (t, J 6.9 Hz, 1H), 7.05-7.41 (m, 8H), 7.52-7.57 (m, 2H)
		m/z	325 (38%), 324 (100), 323 (12), 149 (13), 125 (11), 120 (17), 111 (18), 105 (12)
(20g)	-	δH	2.00 (s, 3H), 2.34 (s, 3H), 3.09 (dd, J 10.0 and 6.5 Hz, 1H), 4.43 (dd, J 10.0 and 7.1 Hz, 1H), 6.56 (br t, J 6.8 Hz, 1H), 7.09-7.45 (m, 10H)
		m/z	325 (53 %), 324 (100), 97 (20), 85 (27), 83 (25), 71 (46), 69 (36)
(21g)	-	δH	2.34 (s, 3H), 2.35 (s, 3H), [3.10 (br) and 4.45 (br), 1H)], 6.43 (d, J 6.9 Hz, 1H), 7.10-7.47 (m, 9H), 7.51-7.59 (m, 2H)
		m/z	325 (36%), 324 (100), 323 (13), 85 (12), 71 (18), 69 (13)

properties of the products are given in Table 5 and the isomer ratios of the products in Tables 1 and 2 (the ratios given are the mean of duplicate experiments concordant to ±0.1).

Benzonitrile 3,3-diphenylallyl ylide (16a). A mixture of *N*-benzoyl-3,3-diphenylprop-2-en-1-ylamine **(13a)** (0.51 g, 1.62 mmol) and phosphorus pentachloride (0.53 g, 2.53 mmol) in ether (20 ml) was boiled under reflux under nitrogen for 17 h. The solvent and volatile by-product were removed on the rotary evaporator, first at *ca* 12 mmHg and the at 0.1 mmHg for *ca* 4 h to give a yellow oil, shown by a pilot experiment to be *N*-(3,3-diphenylprop-2-en-1-yl)-benzimidoyl chloride δH 4.37 (d, J 7Hz, 2H), 6.25 (t, J 7 Hz, 1H), 7.20-7.43 (m, 13H), 7.87-8.10 (m, 2H). The oil was dissolved in THF (10 ml) and potassium *tert*-butoxide (0.56 g, 5.0 mmol) was added with magnetic stirring in one batch at room temperature. A deep purple colour was generated at once which faded after *ca* 15 min. After 2 h at room temperature aqueous ammonium chloride (sat.) (10 ml) was added and the mixture was extracted with ether (2 x 10 ml). Separation, drying and evaporation of the organic phase gave an oil. Flash chromatography on 10% deactivated neutral alumina (petroleum ether : ether 100 : 0 -> 50 : 50) and crystallisation from petroleum ether (b.p. 60-80°C) / toluene gave *1,5-diphenyl-3*H-*2-benzazepine* **(19)** (0.35 g, 73%), m.p. 137-139°C (Found : C, 89.7; H, 5.9; N, 4.4. $C_{22}H_{17}N$ requires C, 89.5; H, 5.80; N, 4.7%). A picrate derivative was prepared and crystallised from ethanol, m.p.173-175°C (Found : C, 64.2; H, 4.1; N, 10.4. $C_{28}H_{20}N_4O_7$ requires C, 64.1; H, 3.8; N, 10.7).

Benzonitrile 3,3-bis(3'-methylphenyl)allyl ylide (16b). The amide **(13b)** (0.13 g, 0.37 mmol) and phosphorus pentachloride (0.12 g, 0.57 mmol) in ether (20 ml) / reflux / 6 h, followed by base (0.20 g, 1.74 mmol) / THF (10 ml) / room temperature for 4 h gave *7-methyl-5-(3'-methylphenyl)-1-phenyl-3*H-*2-benzazepine* **(21b)** and *9-methyl-5-(3'-methylphenyl)-1-phenyl-3*H-*2-benzazepine* **(20b)** (0.11 g, 89%) as an orange oil (Found m/z 323.1663. $C_{24}H_{21}N$ requires m/z 323.1674).

Benzonitrile 3,3-bis(3'-methoxyphenyl)allyl ylide (16c). The amide **(13c)** (0.048 g, 0.13 mmol) and thionyl chloride (0.1 ml) in perdeuteriotetrahydrofuran (0.3 ml) / room temperature / 41.5 h with n.m.r. monitoring, followed by base (0.021 g, 0.19 mmol) / THF (3 ml) / room temperature for 2 h gave *7-methoxy-5-(3'-methoxyphenyl)-1-phenyl-3*H-*2-benzazepine* **(21c)** and *9-methoxy-5-(3'-methyoxyphenyl)-1-phenyl-3*H-*2-benzazepine* **(20c)** (0.041 g, 89%) as an orange oil (Found m/z 355.1571. $C_{24}H_{21}NO_2$ requires m/ z 355.1572).

Benzonitrile 3,3-bis(3'-trifluoromethylphenyl)allyl ylide (16d). The amide **(13d)** (0.074 g, 0.16 mmol) and thionyl chloride (0.15 ml) in perdeuteriotetrahydofuran (0.3 ml) / room temperature / 21 h with n.m.r. monitoring, followed by base (0.031 g, 0.28 mmol) / THF (2 ml) / 0°C for 0.5 h gave *1-phenyl-9-(trifluoromethylphenyl)-3*H-*2-benzazepine* **(20d)** and *1-phenyl-7-(trifluoromethylphenyl)-3*H-*2-benzazepine* **(21d)** as an orange oil (Found m/z 431.1101. $C_{24}H_{15}NF_6$ requires 431.1109) (79%) and recovered amide **(13d)** (21%).

Benzonitrile 3,3-bis(3'-chlorophenyl)allyl ylide (16e). The amide **(13e)** (0.091 g, 0.24 mmol) and thionyl chloride (0.5 ml) in THF (1 ml) / 17 h / room temperature, followed by base (0.047 g, 0.42 mmol) / THF (3 ml) / 0°C for 0.5 h gave *7-chloro-5-(3'-chlorophenyl)-1-phenyl-3*H-*2-benzazepine* **(21e)** and *9-chloro-5-(3'-chlorophenyl)-1-phenyl-3*H-*2-benzazepine* **(20e)** (0.087 g, 100%) as an orange oil (Found m/z 363.0573. $C_{22}H_{15}NCl_2$ requires 363.0581).

Benzonitrile 3,3-bis(2'-deuterio-3'-methylphenyl)allyl ylide (16f). The amide **(13f)** (0.076 g, 0.22 mmol) and thionyl chloride (0.15 ml) in perdeuteriotetrahydrofuran (0.3 ml) / room temperature / 41 h with n.m.r monitoring (*ca* 29% amide remained after 40 h), followed by base (0.040 g, 0.36 mmol) / THF (2 ml) / 0°C for 1 h gave a mixture of *3-deuterio-5-(2'-deuterio-3'-methylphenyl)-9-methyl-1-phenyl-3*H-*2-benzazepine* **(20f)** and *6-deuterio-5-(2'-deuterio-3'-methylphenyl)-7-methyl-1-phenyl-3*H-*2-benzazepine* **(21f)** as an orange oil (0.035 g, 49%), ^{2}H n.m.r. (76.21 MHz, $CHCl_3$) δ 3.1, 4.4, 7.2; integral ratio aromatic/aliphatic=1.97 and 1.75 for two experiments. This product and that of a duplicate reaction were combined and the isomers were separated by chromatography to give **(20f)** as a yellow oil (19 mg) (Found m/z 325.1799. $C_{24}H_{19}{}^2H_2N$ requires 325.1799) and **(21f)** as a yellow oil (7 mg) (Found m/z 325.1806. $C_{24}H_{19}{}^2H_2N$ requires 325.1799).

Benzonitrile 3,3-bis(6'-deuterio-3'-methylphenyl)allyl ylide (16g). The amide (**13g**) (0.078 g, 0.23 mmol) and thionyl chloride (0.5 ml) in ether (1.5 ml) / reflux /17 h followed by base (0.042 g, 0.37 mmol) / THF (4 ml) / room temperature / 1 h gave a mixture of *6-deuterio-5-(6'-deuterio-3'-methylphenyl)-9-methyl-1-phenyl-3H-2-benzazepine* (**20g**) and *3-deuterio-5-(6'-deuterio-3'-methylphenyl)-7-methyl-1-phenyl-3H-2-benzazepine* (**21g**) as an orange oil (0.027 g, 37%), ^{2}H n.m.r. (76.21 MHz, $CHCl_3$) δ 3.3, 4.4, 7.1; integral ratio aromatic/aliphatic=4.56 and 5.61 for two experiments.. This product and that of a duplicate reaction were combined and the isomers were separated by chromatography to give (**21g**) as a yellow oil (2.4 mg) (Found m/z 325.1805. $C_{24}H_{19}{}^2H_2N$ requires 325.1799) and (**20g**) as a yellow oil (11 mg) (Found m/z 325.1784. $C_{24}H_{19}{}^2H_2N$ requires 325.1799).

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